dyes in very heterogeneous fashion. In particular, hair ends damaged by previous treatments, e.g., perming or by air, sun, and so on, will be much more receptive than the roots or shafts. The hair ends can be "choosy" and selective, absorbing some dyes preferentially and rejecting others, while the shafts behave differently.

This phenomenon of selectivity has several aspects to watch out for:

1. Selectivity in substantivity, which might be responsible for different colorings on different portions of the same, individual hair
2. Selectivity in the way the colorants hold, leaving, after several days, unforeseen shades
3. Selectivity in chemical behavior vis-à-vis permanent wave lotions: certain dyes can thus be destroyed or changed by the reducing action of thioglycollates, whereas others are able to resist

A simple case illustrating possible disadvantages is the following: A chestnut shade may be obtained by mixing a nitro compound dye like 1,4-diamino-2-nitrobenzene (2-nitro-*p*-phenylenediamine), red-orange, with a basic dye green, such as malachite green. If the hair ends have been damaged, they may selectively absorb the green dye, while the roots will absorb the chestnut color produced by the mixture. But if the entire head of hair takes on a homogeneous tint, the unstable basic dye shade will inevitably fade at a rapid rate under the action of light. The highlight will then deepen, and the process will probably produce uneven results along the hair shaft. Unfamiliarity with this crucial information has led to serious failures.

In order to avoid selectivity in its various manifestations, efforts should be directed toward using dyes of the same chemical class. Even this is not enough however: their basic qualities should also be very nearly identical, so that their affinity for hair and chemical behavior will be of the same order.

Unfortunately, it is often necessary to use dyes belonging to different chemical classes. Consequently, one can expect to meet the shortcomings described previously. Laboratory tests cannot predict all eventualities, and only application to a large number of heads in all possible technical conditions can give the information required in estimating possible mishaps.

Stability in Solution

This is included as a reminder; but the chemist concerned with product development will regard this as of primary importance.

B. Possible Chemical and Physicochemical Systems

The development of a simple product is a complicated process. In-depth study of systems is carried out in response to the great demand for semipermanent dyes and the multiplicity of their possible applications. Manufacturers' experience and detailed examination of existing products and patent literature is the key to the

development of formulation procedures. The chemical classes in these procedures are sometimes sufficient for homogeneous formulation, but within a single formulation there are often several chemical groups of dyes.

Nitrobenzene Dyes

These include aromatic amines, aminophenols, and nitrophenols. Adding one or more nitro groups to the benzene ring gives the molecule a dyeing potential even in the absence of oxidant. These dyes have a remarkable affinity for hair keratin. Simultaneously, these substitutions on the ring generally eliminate the possibility of oxidative condensation. The nitrobenzene derivatives are not, as a general rule, oxidation dyes but true, direct dyes.

This class features a great number of yellow, orange, and red dyes. Multiple substitutions, performed in particular on the amino groups attached to the ring, yielded pink, purple-violet, violet, violet-blue colors. Cosmetic chemists have a wealth of shades at their fingertips, providing an impressive formulation potential.

Substituting the hydrogen atoms of the amino groups by radicals such as the following results in a deepening of the shades (bathochromic effect, i.e. shift toward longer wavelengths).

CH_3 or CH_2CH_3	$CH_2CH_2NH_2$
CH_2CH_2OH	$CH_2CH_2\text{-}N\begin{matrix} R \\ R' \end{matrix}$
$CH_2CHOHCH_2OH$	CH_2CONH_2
$CH_2CHOHCH_3$	CH_2COOH

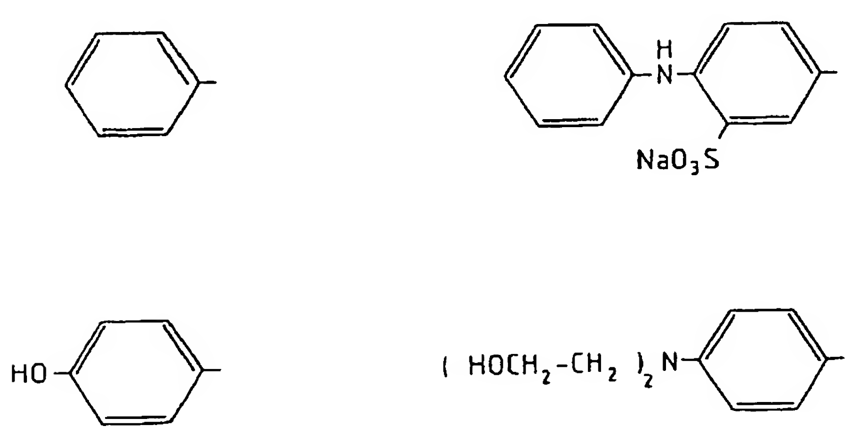
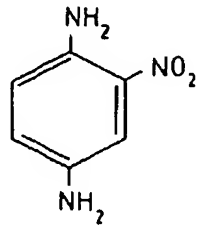


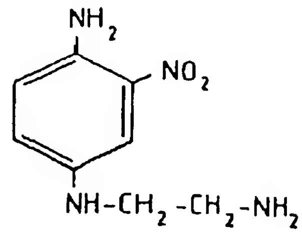
Figure 3

This is how the red-orange, for example, of the 1,4-diamino-2-nitrobenzene becomes violet-purple and even violet:



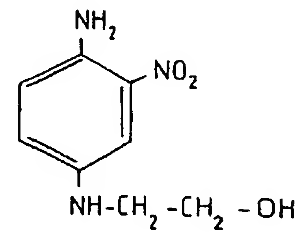
1,4 - Diamino - 2 - nitrobenzene
Red Orange

(I)



1 - Amino - 2 - nitro - 4 - β - aminoethylaminobenzene
Red Purple

(II)



1 - Amino - 2 - nitro - 4 - - β - hydroxyethylaminobenzene
Red Purple

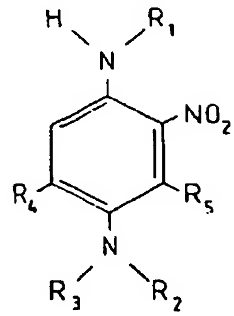
(III)

This deepening of color is often accompanied by a decrease in keratin affinity. But as in the case of certain substitutions, there is an increase in solubility. The decrease can be compensated for by using a higher concentration. The basic or acid character of the radicals introduced also modifies the tinting characteristics, according to the pH at use.

The following classification gives a proposed nomenclature for some of the main dyes in use:

Nitro derivatives of 1,4-diaminobenzene (IV *a–m*, Table 1)

1,4-Diamino-2-nitrobenzene,	*Orange-Red*
1-Amino-2-nitro-4-β-hydroxyethylamino-benzene	*Purple-Red*
1-Amino-2-nitro-4-bis-(β-hydroxyethyl)-amino-benzene	*Red-Violet*
1,4-bis-(β-hydroxyethyl)amino-2-nitro-benzene	*Violet*
1-β-Hydroxyethylamino-2-nitro-4-bis-(β-hydroxyethyl) amino-benzene (HC Blue 2)	*Blue-Violet*
1-Methylamino-2-nitro-4-bis-(β-hydroxyethyl)amino-benzene (HC Blue 1)	*Purple-Blue*
1-β-Hydroxyethylamino-2-nitro-4-amino-benzene (HC Red 3)	*Purple-Red*
1-Methylamino-2-nitro-4-(Methyl,β-hydroxyethyl)amino-benzene	*Blue-Violet*
1-Amino-2-nitro-4-β-hydroxyethylamino-5-methyl-benzene	*Purple-Red*
1-Amino-2-nitro-4-β-hydroxyethylamino-5-chloro-benzene	*Purple-Red*
1-Amino-2-nitro-4-β-aminoethylamino-3-methyl-benzene	*Red*
1-β-Aminoethylamino-2-nitro-4-bis-(β-hydroxyethyl)amino-benzene	*Blue-Violet*
1-Amino-2-nitro-4-methylamino-benzene	*Red*



(IV)

Table 1

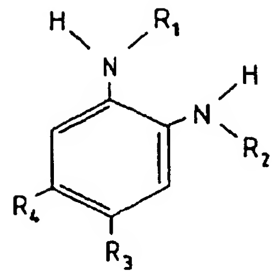
	R_1	R_2	R_3	R_4	
a.	H	H	H	H	*Orange-Red*
b.	H	H	CH_2-CH_2OH	H	*Purple-Red*
c.	H	CH_2-CH_2OH	CH_2-CH_2OH	H	*Red-Violet*
d.	CH_2-CH_2OH	H	CH_2-CH_2OH	H	*Violet*
e.	CH_2-CH_2OH	CH_2-CH_2OH	CH_2-CH_2OH	H	*Blue-Violet*
f.	CH_3	CH_2-CH_2OH	CH_2-CH_2OH	H	*Purple-Blue*
g.	CH_2-CH_2OH	H	H	H	*Purple-Red*
h.	CH_3	CH_3	CH_2-CH_2OH	H	*Blue-Violet*
i.	H	H	CH_2-CH_2OH	CH_3	*Purple-Red*
j.	H	H	CH_2-CH_2OH	Cl	*Purple-Red*
k.	H	H	CH_2-CH_2OH	CH_3	*Red*
l.	CH_2-CH_2OH	CH_2-CH_2OH	CH_2-CH_2OH	H	*Blue-Violet*
m.	H	H	CH_3	H	*Red*

Nitro derivatives of 1,2-Diaminobenzene (V *a–d*, Table 2)

1,2-Diamino-4-nitro-benzene, *Orange-Yellow*
1-Amino-2-β-hydroxyethylamino--5-nitro-benzene (HC Yellow 5), *Yellow-Orange*
1,2-di-(β-hydroxyethylamino)-4-nitro-benzene, *Yellow-Orange*
1-Amino-2-tris-(hydroxymethyl) methylamino-5-nitro-benzene, *Orange-Yellow*

Nitro derivatives of aminophenols or O-substituted aminophenols (VI *a–i*, Table 3)

1-Hydroxy-2-amino-5-nitro-benzene, *Yellow*
1-Hydroxy-2-amino-4-nitro-benzene, *Orange-Brown*
1-Hydroxy-3-nitro-4-amino-benzene, *Orange*
1-Hydroxy-2-amino-4,6-dinitro-benzene, *Orange*
1-β-Hydroxyethyloxy-2-β-hydroxyethylamino-5-nitro-benzene (HC Yellow 4), *Green-Yellow*
1-Hydroxy-2-amino-3-nitro-benzene, *Orange-Yellow*
1-Methoxy-2-β-hydroxyethylamino-5-nitro-benzene, *Green-Yellow*
1-β-Hydroxyethyloxy-3-methylamino-4-nitro-benzene, *Green-Yellow*
1-β-Aminoethylamino-2-nitro-4-β-hydroxy-ethyloxy-benzene, *Orange*



(V)

Table 2

	R_1	R_2	R_3	R_4	
a.	H	H	NO_2	H	*Orange-Yellow*
b.	H	CH_2-CH_2OH	H	NO_2	*Yellow-Orange*
c.	CH_2-CH_2OH	CH_2-CH_2OH	NO_2	H	*Yellow-Orange*
d.	H	$C(CH_2OH)_3$	H	NO_2	*Orange-Yellow*

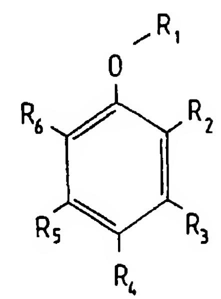
Solvent-Assisted Dyeing Systems

Semipermanent or direct dyeing using carefully selected organic solvents is the adaptation to hair coloring of techniques researched for textile-fiber dyeing.

Solvents such as glycol ethers, cyclohexanol, furfuryl alcohol, benzyl alcohol, and phenethyl alcohol increase the affinity for hair keratin in low-substantivity dyes under normal conditions of use. These solvents can be miscible in water in any proportion, like butyl ether of ethylene glycol (butylcellosolve) or of relatively low solubility, like benzyl alcohol or the hexyl ether of ethylene glycol. These solvents work at optimum concentrations, and when they are poorly miscible with water, the optimum level can be the limit of solubility.

It is not well understood how these solvents work, but it is generally accepted that they facilitate the absorption of dyes onto the surface of the hair fiber. The accelerating effect of the solvents seems to be closely related to their dielectric constant. Although it is unwise to assume that the efficiency of the solvent increases as the constant decreases, observation shows that promising results are only obtained through the use of solvents with a dielectric constant lower than 15 (at 25 °C) (Table 4).

The use of this kind of solvent makes it possible to effect direct dyeing with a number of dyes with solubility characteristics and chemical structure that, at first glance, might seem inadequate.



VI

Table 3

	R_1	R_2	R_3	R_4	R_5	R_6	
a.	H	NH_2	H	H	NO_2	H	*Yellow*
b.	H	NH_2	H	NO_2	H	H	*Orange-Brown*
c.	H	H	NO_2	NH_2	H	H	*Orange*
d.	H	NH_2	H	NO_2	H	NO_2	*Orange*
e.	CH_2-CH_2OH	NH-CH_2-CH_2OH	H	H	NO_2	H	*Green-Yellow*
f.	H	NH_2	NO_2	H	H	H	*Orange-Yellow*
g.	CH_3	NH-CH_2-CH_2OH	H	H	NO_2	H	*Green-Yellow*
h.	CH_2-CH_2OH	H	NH-CH_3	NO_2	H	H	*Green-Yellow*
i.	CH_2-CH_2OH	H	NO_2	NH-CH_2-CH_2-NH_2	H	H	*Orange*

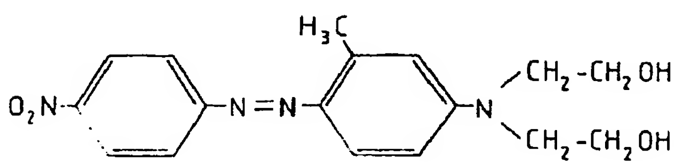
Table 4 Dielectric Constants and Solvent Contribution to (direct) Dye Uptake

Solvent	Dielectric constant	Contribution
Furfuryl alcohol	2.7 at 25 °C	Excellent
Tert-amyl alcohol	5.8 at 25 °C	Satisfactory
Ethyl acetate	6.0 at 25 °C	Very good
Ethyl formate	7.1 at 25 °C	Very good
Butylcellosolve	9.4 at 20 °C	Excellent
Butylcarbitol	10.7 at 20 °C	Satisfactory
Tert-butyl alcohol	10.9 at 20 °C	Good
Phenethyl alcohol	12.3 at 20 °C	Good
Benzyl alcohol	13 at 20 °C	Satisfactory
Cyclohexanol	15 at 25 °C	Satisfactory
2-butanol	15.8 at 25 °C	Satisfactory

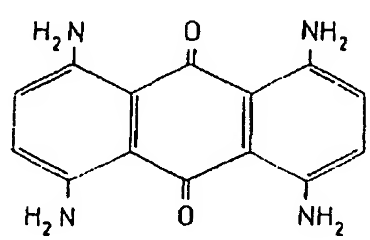
This system is promising in particular for two classes of dye: the disperse dyes and the metallic dyes.

The disperse dyes are not readily soluble in water. They are reduced to extremely fine particles and maintained in suspension by a dispersing agent until absorption by the fiber takes place. The disperser is often a surfactant similar to condensation products of naphthalene sulfonic acids with formaldehyde.

In this class are a large number of azo and anthraquinone dyes. Two examples are shown.



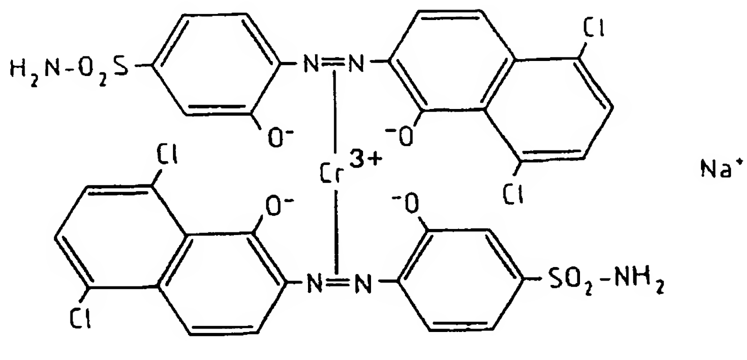
(VII)



C I 64500 - Disperse Blue 1

(VIII)

The metallic dyes are of even greater interest. These are metallic complexes in which all the coordination numbers of the metal are saturated. The characteristic properties of the metallic ion then disappear. The compound (IX) is representative of such azo metal complexes.



C I Acid Blue 170

(IX)

These dyes are of some interest for hair dyeing only if they are used with solvents selected with the utmost care, which will ensure good affinity at room temperature.

They are derived from azo dyes, which means that their color possesses the richness of the azo dye range. But introducing the metal atom "flattens" the shades, dulls them. This last feature is of special importance in the case of hair coloring.

Since the N = N group is being in a way blocked, these dyes are very stable in solution and are highly stable to sunlight.

Metallic dyes are particularly suitable for the adjustment of grey or natural shades, as some of them are homogeneous greys or browns.

Anion-Cation Complexes

The advantages of cationic agents have always been attractive in relation to affinity, as a possible means of facilitating dye adsorption onto the keratin fiber. A two-step operation has actually been proposed: first, treatment of the hair by a cationic surfactant, followed by application of an acid dye solution. But this kind of operation is too complicated.

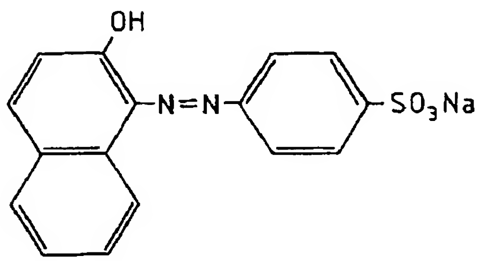
The properties of a great many acid dyes can be considerably modified by forming a complex with a cationic surfactant derivative. If the proportions are stoichiometric, an anion-cation complex is obtained, which acts as a new dyestuff, but is generally insoluble. It is essential to disperse it or solubilize it using a surface-active agent, most often a nonionic compound. The anion-cation

complex put in solution can entail much better affinity for hair keratin than the initial acid dye.

The dyestuffs especially well suited to this sort of formulation are as mentioned, the acid dyes, that is to say, those having essentially the function SO_3H or COOH in their molecular structure. Among them are the following:

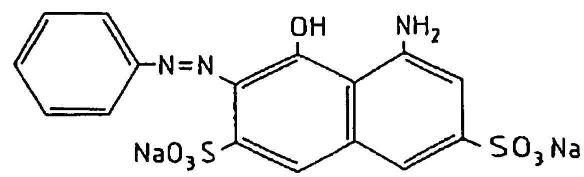
Azoic Acid Dyes.

e.g. CI 17200 (Acid Red 33)
CI 15510 (Acid Orange 7)
CI 13065 (Acid Yellow 36)



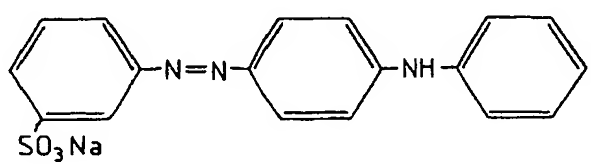
Acid Orange 7

(X)



Acid Red 33

(XI)



Acid Yellow 36

(XII)

Azinic Dyes.

Indulines, e.g., CI Acid Blue 20
Nigrosines, e.g., CI Acid Black 2

The surface-active agents are of the quaternary (quaternary ammonium, pyridinium, quinolinium) or tertiary amine-type.

The nonionic surfactants used in redissolving the stoichiometric complex include fatty ethoxylated alcohols, ethoxylated alkylphenols, etc. They can be associated with or replaced by solvents like the glycol ethers (ethylcellosolve, butylcellosolve, etc.).

If the cation-active product is itself sufficiently ethoxylated, it can assume the double function of cationic complexing agent and solvent for the anion–cation complex.

The formulation of anion-cation dye compounds is difficult and must fulfill two requirements:

1. The complex must be precisely equimolecular for maximum affinity
2. The complex must be precisely redissolved by the nonpolar solvent

If the amount of the latter is insufficient, the anion-cation complex "sticks" to the fiber, thus yielding opaque, very irregular patches that are not resistant to friction. If the amount is excessive, affinity decreases considerably; the partition coefficient of the anion-cation dye favors solubility at the expense of the hair shaft.

The anion-cation complexes are of especial note, because they give acid colorants with low affinity a significantly increased affinity for hair keratin. This is particularly useful for the formulation of semipermanent grey rinses to be applied on white hair. It is a fact that the different forms of selectivity are very evident in white hair, and the best way to avoid them is to avoid dye mixes in formulations. But homogenous greys are rare. There are some among the metallic dyes; their affinity can be increased using the solvent system. Others can be found in the series of azinic dyes like the Induline or Nigrosine dyes, which are generally sparingly soluble; their solubility can be augmented by introducing $-SO_3H$ groups in their molecular structure. Thus, it is possible to obtain soluble, homogeneous greys that still have low affinity for the hair. The anion-cation system gives them affinity.

Anion-cation complexes offer a second advantage in that they may produce even coloring of the fiber, which is relatively rarely achieved. Yet, inherent in their use lies a disadvantage: They work by absorption, i.e., by a surface phenomenon. This casts doubt on their fastness. Nonetheless, the fastness of Nigrosines and Indulines is sufficient to be able to use the term semipermanent dye—the shades stand up to friction (they do not come off on collars or pillowcases) and sun, and persist through several shampoos. But the fastness relies on the strength of the initial acid dye, and it is clear that the anion-cation system also helps in the formulation of temporary dye products (see Sec. V).

Promising results have also been obtained using cationic dye–anionic surfactant, or anionic dye–cationic dye combinations. In practice, however, the former has proved the most useful, if only because it retains the properties contributed by the cationic surfactant: acidic pH, easy disentangling, hair softness, etc.

Self-Oxidizing Dyes

Numerous organic molecules, aromatic amine or aminophenol derivatives, are capable of self-oxidation in contact with atmospheric oxygen, and thus yield colored polymers and dyes. But in most cases, oxidation by air contact leads to unstable, intermediate compounds: The oxidizing polymerization continues and, for that reason, the hair shade will continue to evolve, sometimes with dramatic

end results. Triaminobenzene does this, rapidly producing a nice black-blue color on a head of hair at room temperature. It is so unstable, however, that after several days a red shade emerges. A similar though less eye-shocking result occurs with *m*-diaminophenol: In contact with atmospheric oxygen the original light-chestnut shade will turn to chestnut-auburn after several days. Stable shades can only develop after intense oxidation, which explains why its correct place is in the list of oxidation dyes.

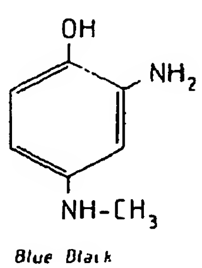
There are, however, a number of molecules, derivatives of polyphenols or aminophenols, that yield, after rapid oxidation, interesting and stable shades that develop on the hair at room temperature. The major ones are derivatives of trihydroxy-benzene, amino-hydroquinone, or 2,4-diaminophenol.

The products are of interest because it is possible by mixing to obtain rather natural tones with fair cover-up intensity, more natural and with a greater covering capacity than the results afforded by the nitro dyes or the other direct dyes in general use (disperse dyes, metallic dyes). The following compounds are some examples:

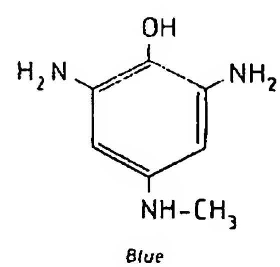
1-Hydroxy-2-amino-4-methylamino-benzene, *blue-black*
1-Hydroxy-2,6-diamino-4-methylamino-benzene, *blue*
1-Hydroxy-2,6-diamino-4-diethylamino-benzene
1,4-Dihydroxy-2-methylamino-benzene (methylamino hydroquinone), *rose auburn*
1,4-Dihydroxy-2-amino-benzene (amino hydroquinone), *green-yellow*

These compounds behave like intermediate derivatives between true dyes and the so-called oxidation dyes.

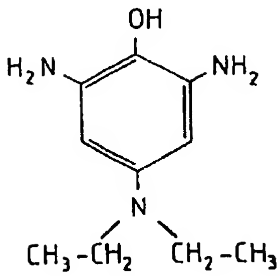
The possibility here exists for the formulation of products, simple and easy to apply, of adequate intensity to conceal white hair in a satisfactory manner.



(XIII)

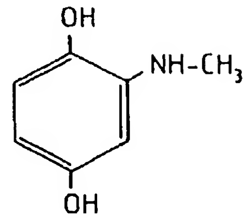


(XIV)



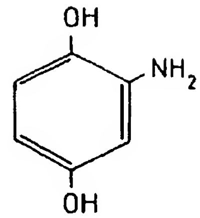
Green

(XV)



Rose auburn

(XVI)

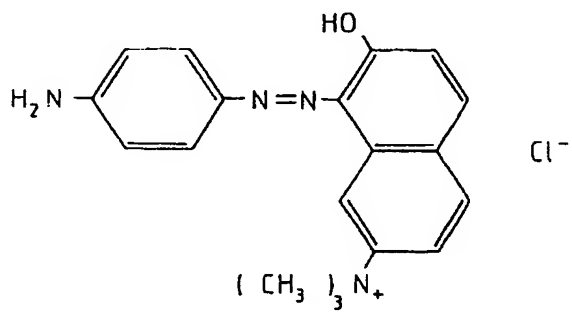


Green yellow

(XVII)

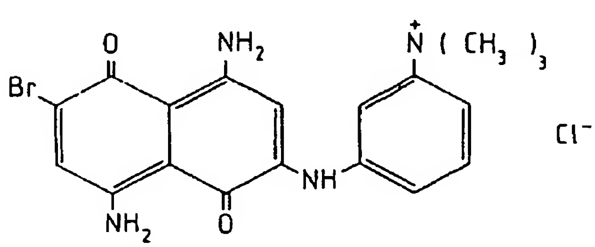
"Arianor" Dyes

These are azo compounds or quinone-imines containing a quaternary group. Being cationic, their affinity for hair keratin is good. a fairly diverse color range allows for homogeneous formulation in all shades. Examples follow:



C I 12250 · Basic Brown 16

(XVIII)



C I 56059 - Basic Blue 99

(XIX)

Formulation must be carried out using a nonionic, amphoteric, or cationic base.

Other Dyes

Many other dyes can be used in the formulation of semipermanent shading products, generally added to correct off-shades. Among them are the following:

Basic Dyes with adequate stability to light. An example is CI 21010 (Basic Brown 4).

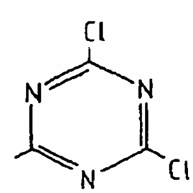
Quaternary Dyes. These are derivatives of amino-anthraquinone such as the following:

1-Amino-anthraquinone
2-Amino-anthraquinone
1-Hydroxy-4-amino-anthraquinone
1-Hydroxy-2,4-diamino-anthraquinone
1,4-Diamino-anthraquinone, etc.

One of the hydrogen atoms of the amino groups is replaced by an ammonioalkyl substituent. In this category are a whole series of highly basic dyes with good affinity for keratin, light-fast and producing shades ranging from yellow to orange, from purple-violet to blue-violet.

Reactive Dyes. These dyes, developed from cellulose fiber-dyeing research, contain a group capable of reacting with the –OH groups of the fiber to yield covalent bonds. The possible reactive groups are numerous. Among the more frequent are the following:

1. Dichloro triazinyl group (XX) (the most reactive, because only traces of water are sufficient to initiate hydrolysis)
2. The chloro amino triazinyl group
3. Groups deriving from chlorinated pyrimidine
4. Vinylsulfones, $-SO_2-CH=CH_2$
5. Acrylamides, $-NHCO-CH=CH_2$ and others



dichlorotriazinyle

(XX)

These reactive groups may be linked to very diverse classes of dye: azo dyes, metallic azo dyes, phthalocyanine derivatives, anthraquinone dyes, etc. It is reasonable to suggest that these dyes will find application in the dyeing of keratin fibers, provided that toxicological properties allow it.

C. Practical Developments of Direct Dye Products

As mentioned previously, direct dye products must help in producing three types of result:

1. Highlights to blend with the natural color of the hair: golden, ash-blond, red, light auburn, dark auburn, purple-violet, etc.
2. The "tone-on-tone" coloring to cover up white hair by tinting it to the natural hair color: blond, light chestnut, chestnut, brown, black, etc.
3. The grey shades designed to rid white hair of yellowish hues and give a grey shade.

Besides these three major types of result, it is possible to brighten up permanently dyed hair shades and to give semipermanent pastel shades to previously bleached hair.

"Party" highlights are generally obtained by using nitrobenzene dyes, especially for the reddish shades.

The "tone-on-tone" colorings can also be done with nitro dyes, as the available dye range goes from yellow to blue. Yet, it is often necessary to deepen the shades by turning to additional dyes belonging to other chemical classes, such as the anthraquinone dyes. Formulation can be effected either with quaternary dyes like the "Arianor" dyes, or with self-oxidizing benzene dyes.

Greys can be obtained with anthraquinone, metallic, azinic, and acid azo dyes. To formulate them, it is often appropriate to use anion-cation complexes.

The semipermanent dyes available to professional hairdressers or directly to the consumer for home use are often products to be applied to the wet hair after shampooing and rinsed out carefully after waiting 10–30 mins. They are available in all kinds of presentation: somewhat disentangling, or foaming lotions, conditioning or foaming creams. Users find the pressurized unit very convenient; it produces the product as a creamy foam (aerosol foam). This means that it is nondrip and easy to apply all through the hair. Semipermanent dyes are sometimes available in shampoo form. The whole process including shampoo, waiting period, and dyeing is thus combined into a single operation. In all cases, the formulation presents numerous difficulties. Formulation requirements imply very strict criteria for dye selection. The remaining problem is achieving perfect compatibility in all areas between the dyes and the various elements in the bases of different products.